

## A NEW ULTRA-VIOLET BAND SYSTEM OF ANTIMONY MONOXIDE (SbO)

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**ABSTRACT.** A new ultra-violet band system, very likely due to a  $^3\Sigma \rightarrow ^1\Pi$  transition, has been photographed under moderately high dispersion in the region  $\lambda 2910 - \lambda 2450$  in the emission spectrum of antimony monoxide. The bands are degraded towards the violet and each band head is itself double. Their vibrational structure analysis shows that the lower state of this new system is identical with that of the other systems already known for the molecule.

### INTRODUCTION

In a recent communication (Sen Gupta, 1939) the vibrational structure analysis of two band systems in the region  $\lambda 6650 - \lambda 3200$  in the emission spectrum of SbO has been described. During this investigation the presence of a number of double-headed bands lying below  $\lambda 3000$  was noticed on the preliminary plates taken with a small quartz spectrograph of large light-gathering power. These bands have not been previously recorded. The analysis of their vibrational structure shows without doubt that their emitter is the diatomic molecule, SbO, inasmuch as the vibrational constants of the lower state of this band system are, within close limits, the same as those of the two existing systems. The object of the present paper is to report the analysis of these new bands.

### EXPERIMENTAL

Using the same light source as previously employed, plates were taken with a Hilger D. I. quartz spectrograph, having a dispersion varying from about 2.2 Å.U per m.m at  $\lambda 2400$  to 4.4 Å.U per m.m at  $\lambda 2900$ . Using iron arc lines as standards of comparison, the wave-lengths of band-heads were measured with a Gaertner precision comparator in the usual way.

### DESCRIPTION OF THE NEW BANDS

As the separation between the sub-levels is very large in comparison to the vibrational spacings, the doublet nature of the system is not apparent at the first sight. The system is, in fact, composed of two sub-systems, the more refrangible and the less refrangible components being indicated by (a) and (b) respectively. The (0, 0) band of the b sub-system is a comparatively strong band at  $\lambda 2663.96$  ( $\nu = 37526.9$ ). The bands (0, 0), (0, 1), (0, 2) and (0, 3) of this

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sub-system are more prominent in comparison to the (1, 0), (2, 0) and (3, 0) bands. In most of the bands the heads appear double evidently due to the P-form and Q-form branches. The separation between these heads increases progressively with increasing  $v'$  - or decreasing  $v''$  - values.

The "a" sub-system also shows similar characteristics with spacings practically identical with those between the bands of the "b" sub-system. It is further found that bands with the same  $v'$ ,  $v''$  - values in the two sub-systems have an interval of approximately  $2272 \text{ cm.}^{-1}$  between them. Thus the  $a(0, 0)$  band is at  $\lambda 2511.89$  ( $\nu = 39798.6$ ). Like the  $b$ -bands, they have also two close heads, the separation between them varying in a similar manner. The bands under consideration may therefore be considered to be made up of two groups, very much identical in their appearance.

### VIBRATIONAL ANALYSIS

Table I gives the wave-lengths in air of all the measured heads and also their wave numbers in vacuo. The  $v'$ ,  $v''$  - values assigned to each band and the type to which its double-heads belong, are also included in the table.

As the Q-form heads are very close to the origins, it may be considered that their wave numbers would represent very approximately the positions of the respective band origins. Hence using the wave number data of the Q-heads, the following equations have been independently derived for the (a) and (b) sub-systems in the usual way.

For the  $b$ -sub-system

$$\nu = 37495.7 + 880.0 (v' + \frac{1}{2}) - 5.80 (v' + \frac{1}{2})^2 - 817.0 (v'' + \frac{1}{2}) + 5.20 (v'' + \frac{1}{2})^2$$

and for the  $a$ -sub-system

$$\nu = 39767.7 + 879.0 (v' + \frac{1}{2}) - 5.90 (v' + \frac{1}{2})^2 - 817.5 (v'' + \frac{1}{2}) + 5.20 (v'' + \frac{1}{2})^2.$$

In table II are given the differences between observed and computed wave-numbers of the band heads.

As the values of  $\omega'_e$  and  $\omega''_e$  do not differ very considerably, the intensity distribution of the bands would lie on a relatively narrow Condon parabola in accordance with the Frank-Condon theory. Although no actual measurement of intensity was made, a visual estimate seems to support the above view. It is further noticed that the Condon parabola in this case has one limb very short while the other limb is comparatively long.

### CORRELATION OF THE BAND SYSTEMS

It may be noted at the very outset that since  $\text{SbO}$  is an odd molecule, its electronic states should be of even multiplicities. The vibrational analysis shows that as one would normally expect, only doublet electronic states are involved in the emission of three observed band systems. The data of their  $\nu_e$ ,  $\omega_e$  and  $\omega_e x_e$  values are collected together in Table III.

TABLE I.

$\lambda$ In air.	$\nu$ In vacuo. in $\text{cm}^{-1}$ .	Assignment.	Type of head	$\lambda$ In air	$\nu$ In vacuo. in $\text{cm}^{-1}$ .	Assignment.	Type of head.
2452.51	40762.2	a(3, 2)	Q	2617.60	38191.5	a(0, 2)	Q
2453.79	40740.9	a(3, 2)	P	2618.90	38172.6	a(0, 2)	P
2455.32	40715.6	a(2, 1)	Q	2651.20	37707.6	b(3, 3)	Q
2456.93	40688.0	a(2, 1)	P	2655.36	37648.5	b(2, 2)	Q
2458.25	40667.0	a(1, 0)	Q	2656.95	37626.0	b(2, 2)	P
2459.59	40645.0	a(1, 0)	P	2659.59	37588.7	b(1, 1)	Q
2493.32	40095.1	b(3, 0)	Q	2661.05	37568.0	b(1, 1)	P
2504.62	39914.2	a(2, 2)	Q	2663.96	37526.9	b(0, 0)	Q
2506.05	39891.4	a(2, 2)	P	2665.93	37504.8	b(0, 0)	P
2508.14	39858.2	a(1, 1)	Q	2666.14	37496.3	a(1, 4)	Q
2509.51	39836.4	a(1, 1)	P	2667.08	37483.0	a(1, 4)	P
2511.89	39798.7	a(0, 0)	Q	2672.64	37405.1	a(0, 3)	Q
2513.19	39778.1	a(0, 0)	P	2711.90	36863.6	b(2, 3)	Q
2542.04	39326.7	b(4, 2)	Q	2717.10	36793.1	b(1, 2)	Q
2544.17	39293.8	b(3, 1)	Q	2721.75	36730.2	a(1, 5)	Q
2545.34	39275.7	b(3, 1)	P	2722.44	36720.9	b(0, 1)	Q
2546.83	39252.7	b(2, 0)	Q	2724.01	36699.7	b(0, 1)	P
2548.63	39225.0	b(2, 0)	P	2729.22	36629.7	a(0, 4)	Q
2554.96	39127.5	a(2, 3)	Q	2776.66	36003.9	b(1, 3)	Q
2559.52	39058.1	a(1, 2)	Q	2778.16	35984.4	b(1, 3)	P
2560.89	39037.2	a(1, 2)	P	2782.78	35924.7	b(0, 2)	Q
2563.84	38992.3	a(0, 1)	Q	2784.15	35907.0	b(0, 2)	P
2565.21	38971.5	a(0, 1)	P	2830.42	35320.1	b(2, 5)	Q
2596.97	38494.9	b(3, 2)	Q	2831.50	35306.6	b(2, 5)	P
2600.30	38445.6	b(2, 1)	Q	2837.50	35231.9	b(1, 4)	Q
2601.57	38426.9	b(2, 1)	P	2838.66	35217.6	b(1, 4)	P
2603.70	38395.4	b(1, 0)	Q	2845.00	35139.1	b(0, 3)	Q
2605.40	38370.4	b(1, 0)	P	2846.09	35125.6	b(0, 3)	P
2606.58	38353.0	a(2, 4)	Q	2900.24	34469.8	b(1, 5)	Q
2611.89	38275.0	a(1, 3)	Q	2909.20	34363.7	b(0, 4)	Q

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TABLE II.

Band.	O-C in $\text{cm}^{-1}$ .	Band.	O-C in $\text{cm}^{-1}$ .	Band.	O-C in $\text{cm}^{-1}$ .
$a(0, 4)$	-2.3	$a(2, 4)$	-1.6	$b(2, 2)$	-0.9
$b(0, 4)$	+0.7	$a(0, 1)$	+1.4	$b(3, 3)$	-1.2
$a(1, 5)$	-3.2	$b(0, 1)$	+0.5	$a(1, 0)$	+1.8
$b(1, 5)$	+3.4	$a(1, 2)$	-3.3	$b(1, 0)$	0.0
$a(0, 3)$	-2.8	$b(1, 2)$	+0.5	$a(2, 1)$	+2.1
$b(0, 3)$	+0.7	$a(2, 3)$	-3.0	$b(2, 1)$	0.0
$a(1, 4)$	-2.0	$b(2, 3)$	0.0	$a(3, 2)$	+1.8
$b(1, 4)$	+0.5	$a(0, 0)$	+0.7	$b(3, 2)$	+0.3
$b(2, 5)$	-3.1	$b(0, 0)$	-0.1	$b(2, 0)$	+0.5
$a(0, 2)$	-2.7	$a(1, 1)$	+0.1	$b(3, 1)$	+3.0
$b(0, 2)$	+0.5	$b(1, 1)$	-0.1	$b(4, 2)$	-1.5
$a(1, 3)$	-0.1	$a(2, 2)$	-2.6	$b(3, 0)$	-3.3
$b(1, 3)$	-2.0				

TABLE III.

Data of  $\text{SbO}$  band systems.

Designation of band system.	$\nu$	$\omega$	$\omega_e'x_e'$	$\omega_e''$	$\omega_e''x_e''$	Region of occurrence
Less Refrangible.	R 20667.5 18528.5	569.0	5.00	817.2	5.38	$\lambda 6650\text{--}\lambda 4500$
More Refrangible	R 26594.0 24322.0	582.0	6.50	817.0	5.40	$\lambda 4720\text{--}\lambda 3245$
New ultra-violet.	V 39767.7 37495.7	879.0 880.5	5.90 5.80	817.5 817.0	5.20 5.20	$\lambda 2910\text{--}\lambda 2450$

The near equality of  $\omega_e''$ — and  $\omega_e''x_e''$ — values indicate that all the three systems have a common lower level. It is further evident that each of the more refrangible and the new ultra-violet systems has a doublet spacing of the same magnitude. One is therefore led to infer that this spacing must be between the doublet components of their common lower level since it is very unlikely that both of them have the same doublet separation in their upper states. The large value of the spacing suggests further that this common lower level is a  $^2\Pi$  state. It may be noted here that in each of the homologous molecules NO, PO

and AsO, the band systems so far discovered have also a common  ${}^2\Pi$  lower level, which is considered to be the ground state of the molecule concerned. In the present case, the common lower level of the band systems may therefore be supposed to represent the ground state of SbO and an interval of  $2272\text{ cm}^{-1}$  between its two  $\Pi$ -components seems also to be of the right order of magnitude.

It is, however, probable that the doublet separations in the upper levels of the above two band systems are too small to be measurable. In that case these upper levels are either  ${}^2\Sigma$  or  ${}^2\Delta$ . Most likely each of them is a  ${}^2\Sigma$  state. The presence of a fairly strong Q-head lends support to this view. It is therefore not unreasonable to suppose that the more refrangible and the new ultra-violet systems are due to transitions between two different excited  ${}^2\Sigma$  states to a common  ${}^2\Pi$  ground state. On the other hand, the less refrangible system has an interval of only  $2139\text{ cm}^{-1}$  between its two sub-systems. This interval is less than that for each of the other two systems by  $133\text{ cm}^{-1}$ . It seems therefore probable that the upper level of these bands has a doublet separation of this value. The absence of double heads as well as the magnitude of the separation suggest further that it is very likely a  ${}^2\Pi$  state. Hence the less refrangible system may be assigned to the transition  ${}^2\Pi \rightarrow {}^2\Pi$ .

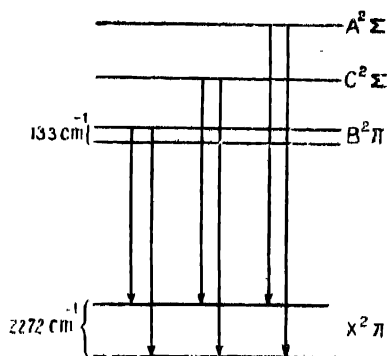


FIG. 1.

The electronic transitions concerned in the emission of the three observed band systems of SbO may be diagrammatically represented as shown in Fig. 1.

It is next of interest to ascertain their analogous band systems in the spectra of the homologous molecules.

#### HOMOLOGOUS SPECTRA

Amongst the homologous monoxides of group V (b) elements, it is well known that NO (Jevons, 1932), which forms the first member of the series, has four overlapping band systems designated as  $\gamma$ ,  $\beta$ ,  $\delta$  and  $\epsilon$  bands and lying in the regions  $\lambda 1665\text{--}\lambda 3460$ ,  $\lambda 2185\text{--}\lambda 5270$ ,  $\lambda 1900\text{--}\lambda 2300$ , and  $\lambda 1670\text{--}\lambda 1880$  respectively. The first three systems appear in the emission spectrum of the molecule. All of them have, however, a common lower level which is the ground state of the molecule. Excepting the bands of the  $\beta$  system, those of

others are degraded to the violet. From an analysis of their rotational structure,  $\gamma$ -bands have been assigned to a transition  ${}^2\Sigma \rightarrow {}^2\Pi$  while  $\beta$ -bands to  ${}^2\Pi \rightarrow {}^2\Pi$ . It is further supposed that  $\delta$ -bands are also due to a  ${}^2\Sigma \rightarrow {}^2\Pi$  transition. The nature of the upper state of the weak  $\epsilon$ -bands, which have been observed in absorption only, is still undecided. The doublet spacing of the two  $\Pi$ -components of the ground level of the molecule has a value of  $121 \text{ cm}^{-1}$ .

In the spectrum of PO, (Ghosh *et al*, 1931, Sengupta *et al*, 1939), so far only two band systems are known. One of them lies in the region  $\lambda 2280 - \lambda 2790$  and is considered as analogous to  $\gamma$ -bands of NO. The second system lies at  $\lambda 3300$  and is supposed to be an analogue of  $\beta$ -bands although it lies on the longer wave-length side of the first system. As one would expect, the doublet separation in the ground level has a higher value than that of NO, and is  $224 \text{ cm}^{-1}$ .

Two systems of bands with a common lower level have been recently analysed by Connelly (1934) and others (Jenkins *et al*, 1935, Morgan *et al*, 1935) in the spectrum of AsO. They are designated as A and B systems and lie in the regions  $\lambda 2950 - \lambda 3450$  and  $\lambda 2350 - \lambda 2800$  respectively. The A system degrades towards the red while the B system towards the violet. Each of them consists of double-headed bands and has been assigned to a  ${}^2\Sigma \rightarrow {}^2\Pi$  transition their ground level having a separation of  $1026 \text{ cm}^{-1}$  between the  $\Pi$ -components. In fact, the A system shows none of the characteristics of a  ${}^2\Pi \rightarrow {}^2\Pi$  transition. Jenkins and Strait (1935) are of opinion that it is the analogue not of the  $\beta$ -bands but of the  $\delta$ -bands of NO while the B system is analogous to the  $\gamma$ -bands. It is thus evident that while in the case of NO the  $\delta$ -bands lie on the shorter wavelength side of the  $\gamma$ -bands, the order is reversed in the spectrum of AsO.

In the spectrum of SbO, the general appearance and intensity distribution of the more refrangible system resemble closely those of A system of AsO. It is therefore very likely analogous to the  $\delta$ -bands of NO. On the other hand the new ultra-violet band system appears to be an analogue of the  $\gamma$ -bands, since it occurs in the expected region of the spectrum. It may be noted here that  $\nu_e$  for the two sub-systems of the  $\gamma$ -bands of NO shifts from  $43965$  and  $43844 \text{ cm}^{-1}$  to  $40489$  and  $40265 \text{ cm}^{-1}$  for PO and to  $40411$  and  $39387 \text{ cm}^{-1}$  for AsO. In the spectrum of SbO,  $\nu_e$  for the new ultra-violet bands is at  $39768$  and  $37476 \text{ cm}^{-1}$ . It is, however, significant that this system becomes weaker in intensity with increasing molecular weight of its emitter. In fact, it is so weakly developed in the spectrum of SbO that one may be led to predict its absence in the spectrum of BiO under similar conditions of excitation. It is further found that the more refrangible and the new ultra-violet systems of SbO are more similar to the A and B systems of AsO than to the  $\delta$  and  $\gamma$  bands of NO as regards their intensity distribution and position. The less refrangible system of SbO is very likely analogous to the  $\beta$ -bands of NO since it bears a close resemblance to the latter in its intensity distribution, besides being due to a similar transition.

A correct vibrational analysis of the bands of BiO is still wanting to make the analogy complete.

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